Peculiarities of critical opalescence for Inhomogeneous liquids under gravity[1]

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ABSTRACT

Experimental and theoretical research of substance properties along susceptibility extremum line for inhomogeneous substance under gravity near the lquid-vapour critical point were carried out in this work. The properties of substance along this line were demonstrated to simultaneously combine properties of system along three limiting critical directions: critical isochor, critical isotherm, phase interface. In the frame of parametrical equation of substance state, the equation of state for substance along the susceptibility extremum line near the liquid-vapour critical point was derived.

KEY WORDS: critical opalescence; critical point; critical temperature, effect of gravity; linear model; order parameter; scale function; susceptibility

1. INTRODUCTION

In researches of high and temperature dependences of the light scattering intensity of inhomogeneous substances near the critical point under gravity an unusual on the face of it the temperature dependences of the light scattering intensity I(t) of substance at different heights $h = \rho_c\, gz\, P_c^{-1} \neq 0$ were discovered [1,2].

Here $t = (T-T_c)/T_c$; T_c , ρ_c , P_c - critical temperature, density and pressure accordingly; g - gravity acceleration; z - a height which is readed from the level where $\rho=\rho_c$.

It turns out that the light scattering intensity of inhomogeneous substances run into own greatest value at these heights no at T but at $T >> T_c$. In [l] the phenomenon theoretical analysis in the frame of phase transition fluctuation theory [3] was made.

Purpose of this work is the continuation of experimental and theoretical researches along this line, definition of substance state equation in the direction of susceptibility extremum curve in the frame of lineal model of state parametrical equation [4].

2.MEASUREMENTS

Temperature dependences of light scattering intensity near the liquid-vapour critical point for freon-113 and binary solution, namely, n-pentan - benzol at different fixed heights have been shown in fig. 1. 2. In these figures symmetrised values $I(z)=1/2\ [\ I(z>0) + I\ (z<0)\ ]$ are shown. Quantities I(z) are taken for the heights that are symmetric about the level z = 0. Measurement were made by device which allows combined investigations the refractometry and the light scattering.

3. RESULTS

During the approach to T_c the light scattering intensity changes unmonotonically at heights h≠0 and one increase monotonically at level h = 0 (Fig.1).

Analysis these and other data [1] show that along susceptibility extremum curve the equilibrium properties of inhomogeneous substances under gravity described by power lows of phase transition fluctuation theory. Critical amplitudes values and critical indices of the power lows for order parameter and susceptibility were determined. On the basis of I(h,t) experimental data for n-pentan [1] and freon-113 [2] parameter $h \cdot t^{-\beta\delta}$ magnitudes in the extremum I(t) points were calculated: $h \cdot t^{-\beta\delta}=0.23 \pm 0.03$. The scaled variable $z_i^* = \Delta\mu_i t_i^{-\beta\delta} = (d\mu^*/dh) h_i t_i^{-\beta\delta} = 32 \pm 2$ was received by considering derivative value $d\mu^*/dh = 140 \pm 20$ [5,6] ($\Delta\mu=(\mu-\mu_c)/\mu_c$, μ_c -critical value of chemical potential).

The variable z also calculated with linear model of parametrical equation of state [4]

$$\Delta\mu = a r^{\beta\delta}\theta(1-\theta^2)$$

$$t = r(1-b^2\theta^2), \qquad (1)$$

$$\Delta\rho = k r^{\beta}\theta .$$

for substance along the susceptibility extremum curve. Thus

$$z_{ì}^{*} = \frac{a\theta_{ì}\left(1-\theta_{ì}^{2}\right)}{\left(1-b^{2}\theta_{ì}^{2}\right)^{\beta\delta}}$$

Parameter θ along the extremum curve

$$\left(\frac{d}{dt}\frac{d\rho}{d\mu}\right)_{h} = \frac{d\beta_{t}(\theta,r)}{dt(\theta,r)} = \frac{\left(d\beta_{t}/d\theta\right)_{r} + \left(d\beta_{t}/dr\right)_{\theta} dr/d\theta}{\left(dt/d\theta\right)_{r} + \left(dt/dr\right)_{\theta} dr/d\theta} = 0$$

was calculated. In case $T > T_c$ [7]

$$\beta_{t} = \frac{k}{a} r^{-\gamma} \frac{1}{1+\left(2\gamma\beta^{2} - 3\right)\theta^{2}}$$

Considering that $\Delta\mu = ar^{\beta\delta}\theta\left(1-\theta^{2}\right) = const$ and critical indices values γ~5/4, β~1/3,δ~5 [3], value θ=0.5 ± 0.08 was obtained. This fact allow to use the model of parametrical equation of substance state in case θ= 0.5 .

It was shown that the substance properties along the extremum curve simultaneousely combine properties of system along three limiting critical directions: critical isotherm ($\theta=b^{-1}$), critical isochor (θ=0), phase interface (θ=1). Susceptibility and order parameter amplitudes in power lows

$$\beta_{tì} = D_{1ì}\left(\Delta\mu\right)^{1/\delta-1}, \qquad \beta_{tì} = \Gamma_{ì}\, t_{ì}^{-\gamma}$$

$$\Delta\rho_{ì} = \hat{A}_{ì}\, t_{ì}^{\beta}, \qquad \Delta\rho_{ì} = D_{2ì}\left(\Delta\mu_{ì}\right)^{1/\delta} \qquad (2)$$

along the curve can be written as

$$\Gamma_{\text{ì}} = \Gamma_0 \frac{\left(1 - b^2\theta_{\text{ì}}^2\right)^{\gamma}}{1 + \left(2\gamma b^2 - 3\right)\theta_{\text{ì}}^2}$$

$$D_{1\text{ì}} = D_{10}\left(\frac{\left(1-\theta_{\text{ì}}^2\right)\left|\theta_{\text{ì}}\right|}{\left(1-b^2\right)b^{-1}}\right)^{1-1/\delta}\frac{1+\left(2\gamma b^2 - 3\right)b^{-2}}{1+\left(2\gamma b^2 - 3\right)\theta_{\text{ì}}^2}$$

$$B_{\text{ì}} = \hat{A}_0\left|\theta_{\text{ì}}\right|\left(\frac{b^2-1}{1-b^2\theta_{\text{ì}}^2}\right)^{\beta},$$

$$D_{2\text{ì}} = D_{20}\left(\frac{1-b^2}{1-\theta_{\text{ì}}^2}\right)^{1/\delta}\left(\left|\theta_{\text{ì}}\right|b\right)^{1-1/\delta}$$

Here Γ_0 , D_{10} are susceptibility amplitudes ; and B_0 , D_{20} are order parameter amplitudes along the lines $\theta=b^{-1}$, $\theta=0$, $\theta=1$. Amplitude values were calculated through numerical values of critical exponents γ, β, δ :

$\Gamma_m/\Gamma_0 = 0.50 \pm 0.08$, $D_{1m}/D_{10} = 1.78 \pm 0{,}45$, $B_m/B_0 = 0.55 \pm 0.08$, $D_{2m}/D_{20} = 0.34 \pm 0{,}08$.

Coefficient **a** was calculated by magnitude of amplitudes D_{20} ($\theta=b^{-1}$) and Γ_0 ($\theta=0$) [4,6-8]

$$a = \left(D_{20}/\Gamma_0\right)^{\delta/(\delta-1)} b\left(1-b^{-2}\right)^{1/(\delta-1)} \qquad (3)$$

and then scaled variable value was estimated with (1), (3) : $z_m^{*/} = 31 \pm 6$.

Obtained results are corroborated by experimental data of high and temperature dependences of the light scattering intensity and refraction index gradient of inhomogeneous individual liquids and binary solutions under gravity near the liquid-vapour critical point.

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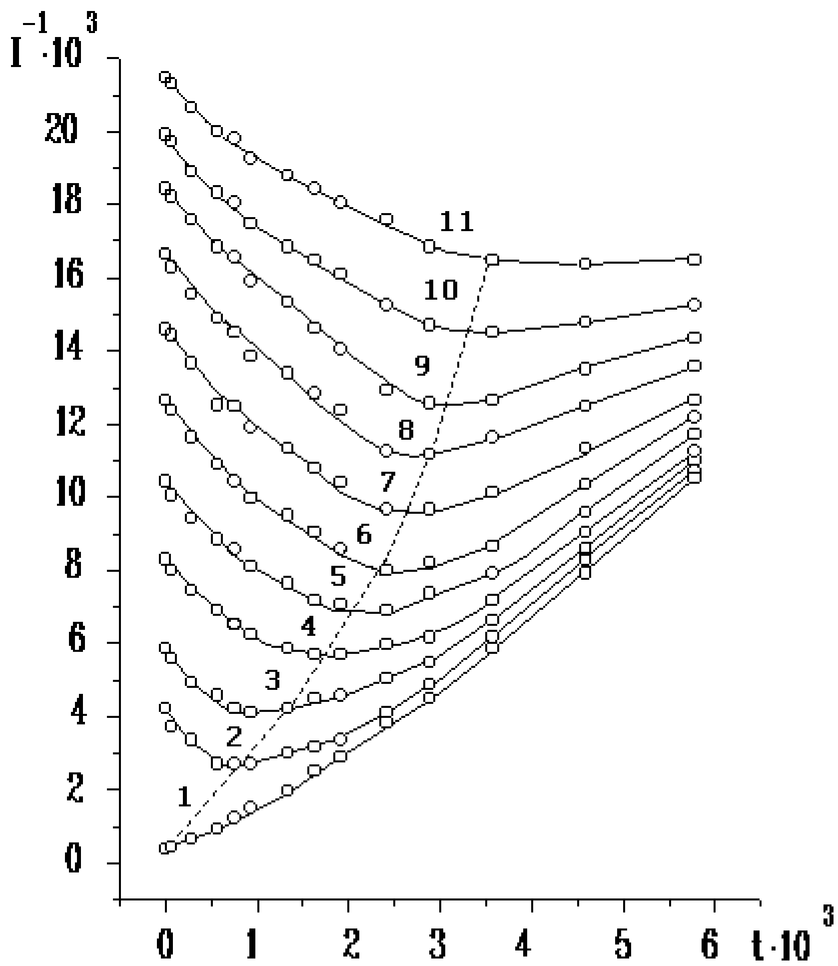
FIGURE CAPTION

Fig.1. Temperature dependences of the reciprocal light scattering intensity in per-unit for freon-113 at fixed heights $z = 2\cdot(n-1)$ mm where $n = 1, 2, \ldots 11$



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